

Hydrometallurgical Molybdenum Recovery from Spent Catalyst Using Tartaric Acid Derived from Agrifood Waste

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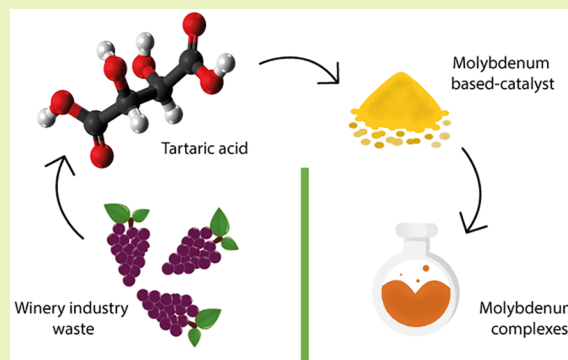
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ABSTRACT: In this study, a green and sustainable hydrometallurgical process, based on soft acid derived from agrifood waste as a byproduct, is used to recover molybdenum from selective spent oxidation catalysts for formaldehyde production. Tartaric acid recovered from winery waste is used as a leaching and chelating agent. The spent catalyst was characterized by X-ray diffraction, scanning electron microscopy, and inductively coupled plasma optical emission spectroscopy. The last term was also used to study the leaching efficiency. Under optimized conditions, a molybdenum recovery of $87.36\% \pm 2.94$ wt % was achieved: 1.3 M tartaric acid, 75 g/L solid–liquid ratio, and 60 min at 25 °C. Moreover, the leaching kinetics were also investigated using the shrinking core model, which is correlated to each step of the leaching process, including chemical reaction, product layer diffusion, and film diffusion control. The step that exhibits the best agreement with the experimental kinetic data is considered as the rate-controlling step. The proposed hydrometallurgical process was found to be simple, efficient, and environmentally friendly. Using agrifood wastes, it becomes possible to process industrial waste to recover and reintegrate expensive metals for an efficient circular economy.

KEYWORDS: spent catalyst, green process, metal recovery, tartaric acid, agrifood waste, kinetic analysis



INTRODUCTION

Molybdenum is used in a variety of industrial and chemical applications, including steel production, lubricants, electrical components, and catalysts.¹ Despite not being classified as a critical raw material by the European Commission in 2023, molybdenum can be considered potentially critical due to its position on the threshold between noncritical raw materials and the criticality zone, with a notably high supply risk score (0.8).² Half of the global molybdenum supply originates from the treatment of molybdenite, powellite, and wulfenite ores, while the remaining 50 percent is obtained as a byproduct during copper smelting.³ At present, molybdenum sulfide concentrate undergoes an initial roasting process on a global scale, leading to its transformation into industrial molybdenum oxide. Subsequently, soluble molybdate salt is extracted from this oxide, which is later used for the smelting of molybdenum metal or its alloys.^{4,5} The focus of this research is on a specific catalyst based on molybdenum to produce formaldehyde, which is an important industrial chemical used in the manufacture of resins, adhesives, and other products. Formaldehyde is typically produced by the catalytic oxidation of methanol. Molybdenum catalysts are often used in this process due to their capability to withstand the high temperatures and pressures required for the reaction. Additionally, they exhibit good activity and selectivity for the production of form-

aldehyde.^{6,7} The formaldehyde market is expected to witness significant growth in the foreseeable future because of various factors such as increasing industrial applications and expanding end-use industries. In Europe it is expected to reach 13.1 million metric tons by 2027.⁸ It is important to focus on these numbers because the production of formaldehyde is proportional to the generation of the spent catalyst. As formaldehyde production increases, a significantly huge proportion of catalyst will be discarded. So, it is crucial and useful to recover the main metal within it. Several hydro- and pyrometallurgical techniques have been proposed to recover molybdenum catalysts.⁹ However, the use of pyrometallurgy processes is somehow restricted to higher energy expenses, secondary environmental impacts like waste gas emissions, and the production of less valuable products like polymetallic alloy.¹⁰ Conversely, hydrometallurgical process approaches are favored for their notable benefits such as reduced energy consumption and lower treatment costs compared to pyrometallurgy.^{10,11}

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Hydrometallurgical processes facilitate the transformation, migration, and enrichment of valuable metals through techniques like low-temperature roasting, strong inorganic or alkali leaching, chemical precipitation, solvent extraction, and ion exchange.¹⁰ However, the main processes use high temperature and strong acids (e.g., H₂SO₄, HNO₃) and bases (e.g., NaOH).¹² To the best of our knowledge, no literature is available regarding the recovery of molybdenum from this type of catalyst, which is extensively utilized in the industry. The recovery of any type of raw material, mainly material with a high supply risk score,² is essential for various reasons. Environmentally traditional metal extraction methods, such as open-pit mining, can cause significant damage to the environment and surrounding ecosystems.¹³ Thus, the recovery process through recycling or other more sustainable methods can reduce the environmental impact of metal production. Additionally, metal recovery requires less energy compared to extracting metals from ore, leading to lower energy consumption and carbon emissions.¹⁴ The Global molybdenum reserve base in 2022 was 12000000 mt, with distribution predominantly from Chile, Peru, U.S.A., and China.⁴ This critical aspect in the supply chain stability and recovering metals from existing sources can help to ensure a stable supply of metals by reducing reliance on a sole ore source (International Molybdenum Association reported that global molybdenum extracted in 2022 was 286440 tonnes from mine production only and does not include material recovered from spent catalysts).¹⁵

In this work, a green and sustainable hydrometallurgical process is developed to recover molybdenum from a spent oxidation catalyst based on tartaric acid. It is a diprotic acid that is found in many plants, particularly in grapes and tamarinds. It has the chemical formula C₄H₆O₆, and it is used in a variety of applications, including food and beverage production, pharmaceuticals, and chemical manufacturing.¹⁶ It is an effective leaching agent for metal extraction because of its ability to form complexes with metal ions.¹⁷ In this study, the recovery was carried out from agrifood waste, specifically from wine lees produced as waste from Italian wineries.^{18,19} According to an estimate provided by the International Organisation of Vine and Wine (OIV), in 2014, 44.4 Mhl of wine were produced in Italy, resulting in 8 million quintals of marc, including grape seeds (equivalent to 15% of grapes vinified), and 2250000 hectolitres of lees (equivalent to 5% of wine produced).²⁰ It is evident that in regions or countries with high wine production, such as Italy, a process that involves the recovery of tartaric acid from winery waste to leach industrial waste becomes feasible. Thus, agrifood waste can be repurposed to treat industrial waste, facilitating the retrieval and reintegration of valuable metal compounds. This practice contributes to the advancement of an effective circular economy where the waste of one process becomes the raw material for another. The goal is to prolong the utilization of resources, extracting their utmost value before they are reclaimed and regenerated.

EXPERIMENTAL SECTION

Materials. Samples of spent catalyst waste were collected from Orim S.p.A., a solid waste recycling company in Marche (Italy). The reagents and chemicals, i.e., nitric acid (69% Hiperpur), and hydrochloric acid (37% puriss) were purchased from PanReac AppliChem and Sigma-Aldrich, respectively, and used as received. Tartaric acid used in this study was sourced from an industry that

recycles wine lees to recover the acid (Distillerie Mazzari S.p.A.) and was used as received. Deionized water was used in the leaching process and to prepare solutions for the analysis.

Characterization Techniques. The concentration of iron and molybdenum in the digested and leach liquors was analyzed using Thermo Scientific iCAP PRO ICP-OES (inductively coupled plasma-optical emission spectrometry). The spent catalyst powder was characterized through XRD (powder X-ray diffraction) using an X Philips PW 1830 generator powder diffractometer employing Cu-K α radiation with wavelength, $\lambda = 1.5418 \text{ \AA}$. Phase identification was made with QUALX2.0.^{21,22} A SEM-EDX, Zeiss Sigma 300 (scanning electron microscopy-energy-dispersive X-ray) instrument was used to study surface morphologies of the spent catalyst and to validate the use of the kinetic model. Microanalysis (C, H, O, N), FT-IR, and TGA-DTA analysis (PerkinElmer STA 6000) were carried out to analyze the presence of humidity and/or organic compounds.

General Procedure. Aqua regia was used to dissolve the samples to measure the total amount of the metals. Specifically, three tests were conducted with the heating plate set at 350 °C. A condenser was used to avoid the evaporation of water. Consequently, the total metal content was calculated as an average of the three trials. For the leaching experiments, a 25 mL round-bottom flask was placed on a magnetic stirrer set at a speed of 300 rpm. The temperature was fixed at 25 or 80 °C (depending on the experiments), and a condenser was used to prevent an increase in tartaric acid concentration. Once the reaction was completed, the solution was filtered and adjusted to the desired volume in a volumetric flask. The metal content of the resulting solution was then measured through ICP-OES. After measuring the metal concentration, the leaching efficiency (LE) of each metal was calculated using eq 1:

$$LE = \frac{[M] \times V \times DF}{wt\%} \times 100 \quad (1)$$

where *M*, *V*, *DF*, and *wt %* are the metal concentrations in leach liquor, the volume of leach liquor, the dilution factor for the ICP-OES analysis, and the mass fraction of metal in spent catalyst powder, respectively. For the ICP-OES analysis (axial mode), calibration curves were created using a series of known concentrations with increasing values (0.001, 0.01, 0.1, 1, and 10 ppm) of molybdenum and iron. The coefficient of determination (*R*²), which represents the goodness of fit of the calibration curve, was required to be greater than 0.990. The relative standard error (RSE), which indicates the precision of the measurements, was kept below 20%. Tartaric acid solution (used as blank in each ICP-OES session) was analyzed by ICP-OES, resulting with a below LOD concentration of iron and molybdenum. The purity of the acid is equal to 99.90%.

RESULTS AND DISCUSSION

Characterization of the Spent Catalyst Powder. Figure 1 shows the XRD pattern of the spent catalyst powder. It exhibits a large amount of amorphous phases and, mainly, the presence of Fe₂(MoO₄)₃ and MoO₃. Commercially available iron molybdate catalysts always contained Fe₂(MoO₄)₃ and MoO₃.^{6,7} Knowing the crystalline phases present within the catalyst is crucial for understanding the reaction mechanism of tartaric acid during the leaching process and evaluating the acid's capability to dissolve metals that are present in specific crystalline phases.

The QualX software identified nonindexed peaks as organic compounds. The focus of this study is not on identifying the specific organic compounds but rather on confirming their presence. For this reason, detailed information regarding their identification is provided in the SM, where various analyses such as elemental microanalysis (Figure S1), FTIR (Figures S2 and S3), TGA/DTA (Figure S4), and XRD (Figure S5) were conducted. The SEM images in Figure 2 reveal the presence of iron and molybdenum and demonstrate a correlation between

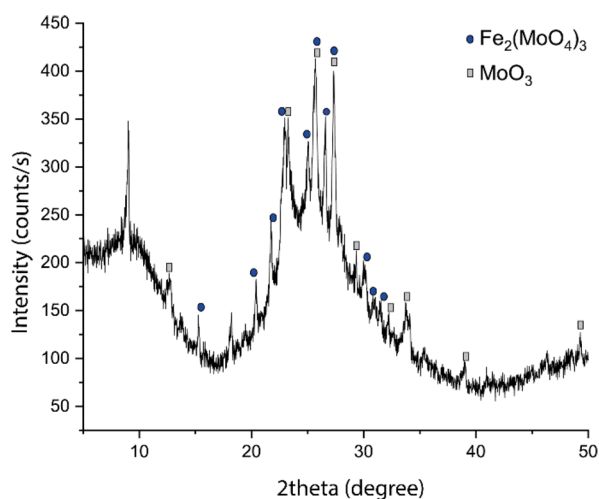


Figure 1. XRD pattern of the spent molybdenum catalyst.

the sites of the two metals. The presence of the $\text{Fe}_2(\text{MoO}_4)_3$ phase and the remaining amount of molybdenum oxide can be confirmed by the ratio of iron to molybdenum in the phase, as confirmed in the SEM-EDX analysis in Table 1.

In this study, SEM analysis was also performed to assess the applicability of the shrinking core model (SCM) and to validate its assumptions, as it relies on the particles maintaining their size and integrity throughout the leaching process.²³ Figure 3 represents SEM images of the spent catalyst powder before the leaching process and the residue remaining after leaching experiments. The images revealed that there is no significant alteration in the particle distribution between the preleaching state (Figure 3a) and the postleaching residue (Figure 3b). Additionally, both images demonstrated the presence of some agglomerates in both cases. These observations suggested that the leaching process did not cause substantial changes in the particle distribution, and it was possible to apply the SCM.

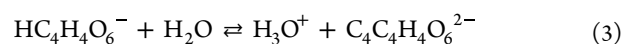
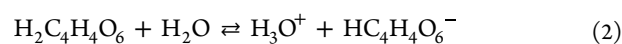
Table 1. EDX Analysis of the Spent Catalyst Powder

element	atom (%)	rel. error (%)
oxygen	82.79	5.12
aluminum	0.44	4.64
calcium	0.06	10.25
iron	5.03	1.40
copper	0.20	4.95
molybdenum	11.48	2.00
sum	100.00	

The total metal content in the spent catalyst was determined through ICP-OES. It measured 58.01 ± 2.71 wt % molybdenum and 13.81 ± 0.54 wt % iron content. All the other metals are below the LOD of the technique, except for aluminum and copper, which account for only 0.5% and 0.03%, respectively, relative to the sum of molybdenum and iron.

Leaching Process and Mechanism. In the leaching process and mechanism, the following factors were investigated: concentration of tartaric acid (0.1–2.5 M), solid–liquid ratio (33–200 g/L), temperature (25–80 °C), and time reaction (1–110 min). Figure 4 showed a graph with the independent variables (solid–liquid ratio, reaction time, and molarity) on the x , y , and z axes at 25 °C. The dependent variable is represented by a color map based on the percentage of molybdenum extracted.

Tartaric acid contains two carboxyl groups in one molecule. Its dissociation reactions (eqs 2 and 4) can be represented as



The $\text{p}K_a$ values of tartaric acid are $\text{p}K_{a1} = 2.72$ and $\text{p}K_{a2} = 4.79$ calculated by MarvinSketch made by Chemaxon. Theoretically, the leaching products can contain Fe^{3+} , Mo^{6+} , or MoO_4^- derived from $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 (see Figure 1).

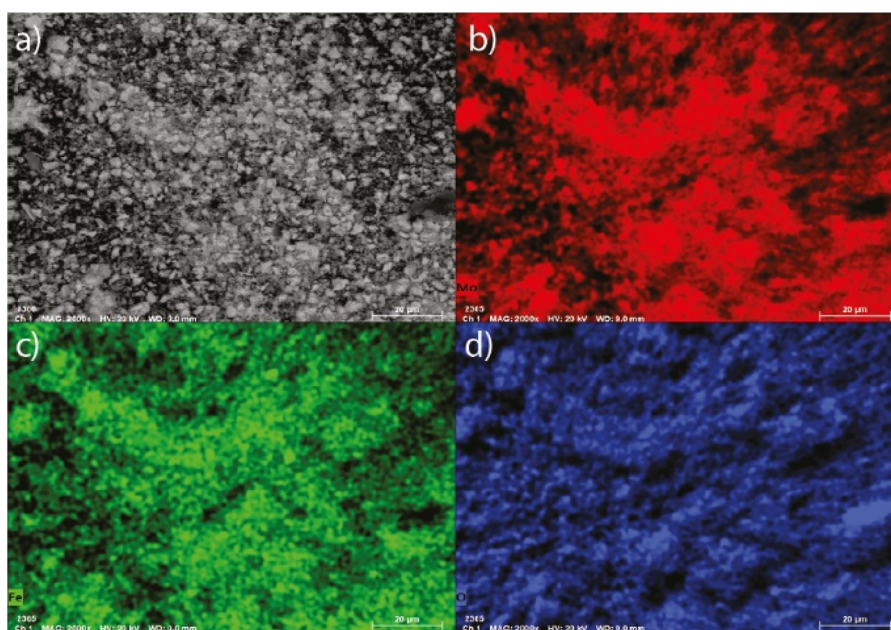


Figure 2. SEM images of spent catalyst powder (a) without EDX map, (b) molybdenum EDX map, (c) iron EDX map, and (d) oxygen EDX map. Magnification 2000 \times and bar = 20 μm .

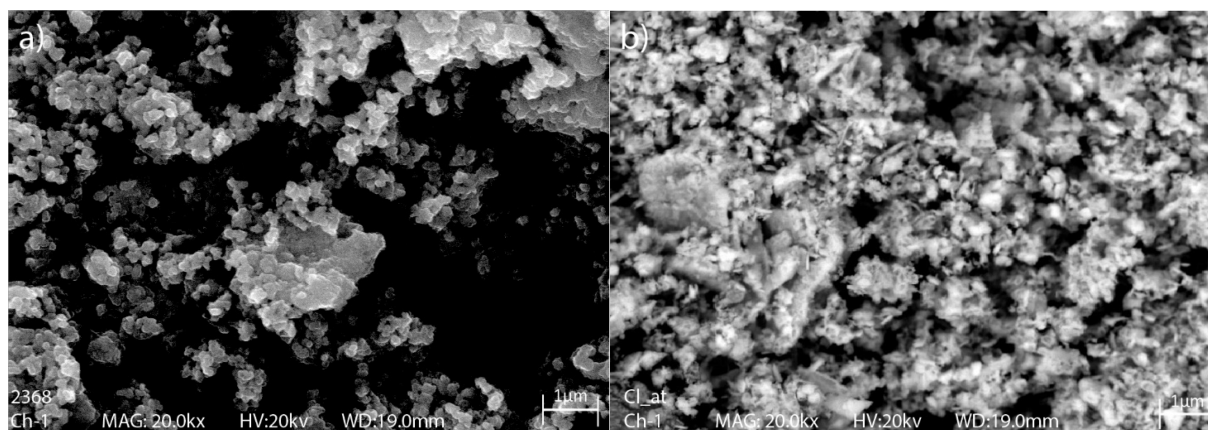


Figure 3. SEM images of the spent catalyst powder (a) before leaching and (b) after leaching; magnification 20.0k \times and bar = 1 μm).

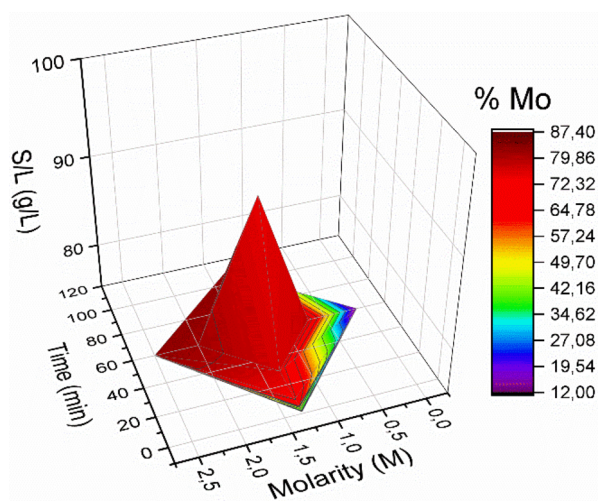
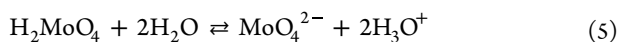


Figure 4. Leaching efficiency of the process (% Mo).

Moreover, MoO_3 can react with water, lowering the pH of the leachate (eqs 4 and 5).²⁴



The leaching process can be understood as a complexation-chelation phenomenon, where the tartaric acid molecules surround and bind to the molybdenum and iron ions, forming a complex compound. Several works have shown the system to be complex and that the nature of species in solution depends upon several factors including pH, temperature, total concentrations, and the M:L ratio, where M are Fe^{3+} , Mo^{6+} , or MoO_4^- species.^{25–29}

Influence of Various Factors on the Leaching Process.

To examine the effect of tartaric acid concentration on molybdenum leaching efficiency, experiments were carried out with variations in tartaric acid molarity of 0.1, 0.7, 1.3, 2.0, and 2.5 M (Figure 5a). The other experimental conditions, i.e., solid–liquid ratio (75 g/L), temperature (25 $^\circ\text{C}$), and reaction time (60 min) were kept constant throughout the experiment. The recovery of molybdenum increased significantly from $12.06 \pm 3.68\%$ at 0.1 M to $87.36 \pm 2.94\%$ with tartaric acid molarity of 1.3 M. This phenomenon can be explained by the fact that a higher concentration of tartaric acid leads to enhance the collision frequency among reactants, consequently

accelerating the reaction rate.¹⁹ Figure 5b shows the effect of the solid–liquid ratio (g/L) on the leaching process. It can be seen that increasing the solid–liquid ratio has a negative effect on the leaching efficiency. This trend is associated with the reduction of the available surface area per unit volume of the solution, which occurs as the solid–liquid ratio increases.³⁰ The amount of spent catalyst powder was varied from 30 to 200 g/L. In this experiment, all other conditions, such as molarity (1.3 M), temperature ($T = 25^\circ\text{C}$), and reaction time (60 min), were kept constant. The leaching efficiency decreases from $87.20 \pm 1.46\%$ to $76.87 \pm 1.61\%$, with the increase in pulp density from 30 to 200 g/L, respectively. The process was optimized to include a solid–liquid ratio of 75 g/L, which resulted in a recovery rate of molybdenum equal to $87.36 \pm 2.94\%$. This value was chosen because it is beneficial in an industrial setting, leading to a lower water consumption, a smaller reactor size, and a smaller solid–liquid separation system. This ultimately reduces the capital and operating expenses of the process. As shown in Figure 5c, the impact of the reaction time on the leaching efficiency of molybdenum was studied under the following conditions: solid–liquid ratio of 75 g/L, temperature of 25 $^\circ\text{C}$, and molarity of 1.3 M. The leaching efficiency of molybdenum was found to increase with the reaction time. Further increasing the reaction time to 110 min resulted in a plateau in leaching efficiency. Thus, 60 min was established as the optimal reaction time for leaching of Mo. A temperature range of 25 to 80 $^\circ\text{C}$ was examined (Figure 5d), with a solid–liquid ratio of 75 g/L and a tartaric acid concentration of 1.3 M, over a 1 h leaching duration to evaluate the impact on the leaching efficiency of molybdenum. Based on the observations in Figure 5d, the recovery of molybdenum shows an insignificant increase from $87.36 \pm 2.94\%$ at 25 $^\circ\text{C}$ to $90.91 \pm 2.90\%$ at 60 $^\circ\text{C}$. Considering cost efficiency in industrial applications, it is preferable to operate at low and room temperature. In this way, energy consumption and associated costs can be reduced, making the process more economically viable. Therefore, for these reasons, the optimal condition was determined to be at room temperature. Generally, higher temperatures promote the leaching reaction because, typically, metal leaching involves an endothermic process.¹⁹ In this case, as can be seen, temperature does not play a significant role in molybdenum extraction.

Black lines represent iron leaching, showing a trend parallel to the molybdenum trend. Thus, tartaric acid is not selective for the molybdenum leaching over iron, and we can observe

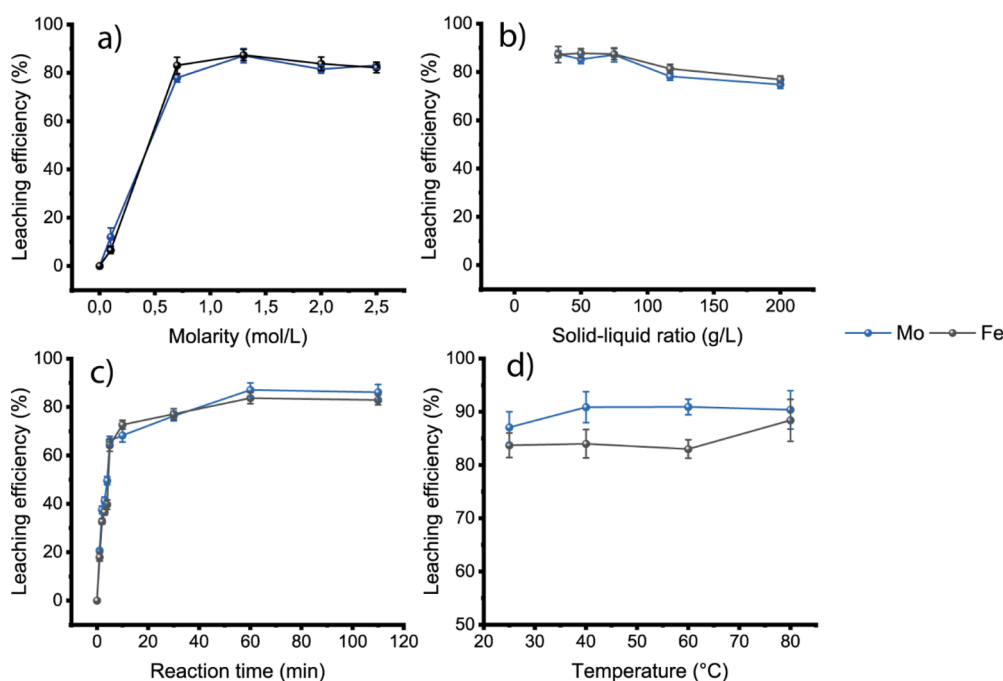


Figure 5. Synoptic graph that shows the effects of each factor on the leaching efficiency: (a) molarity of the tartaric acid, (b) solid–liquid ratio, (c) reaction time, and (d) temperature. In black and blue, respectively, are the iron and molybdenum leaching trends under the same conditions. The error bars indicate the analytical error associated with the leaching process.

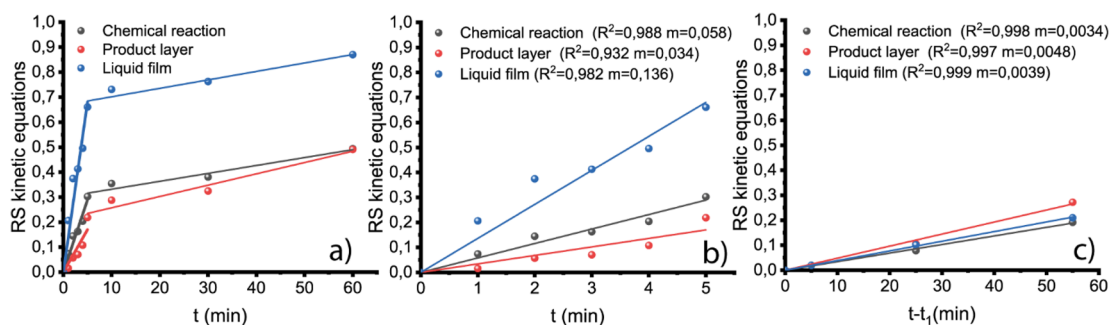


Figure 6. Right side (RS) of rate-controlling equations as a function of time at optimum conditions: (a) eqs 6–8, (b) eqs 6–8 (step 1), (c) eqs 9–11 (step 2).

the same atom ratio (Mo/Fe) in the spent catalyst and in the leachate in the optimized condition.

A series of tests were conducted to recover molybdenum from the solution. To extract molybdenum from the tartrate complexes, an initial attempt was made to precipitate the acid as calcium tartrate at pH 7. Calcium chloride (CaCl_2) was selected for this purpose due to its cost-effectiveness, high solubility, and its ability to precipitate as calcium carbonate (CaCO_3) when exposed to CO_2 , thus obtaining tartaric acid.³¹ This approach would contribute to the reduction of harmful emissions into the environment. To the best of our knowledge, no literature is available on the reuse of tartaric acid after the leaching process. Consequently, molybdenum precipitation can be performed using the conventional method: addition of NH_4Cl , acidification with HCl to achieve pH 2, and heating to 90 °C. This temperature facilitates the formation of precipitates of ammonium molybdate.⁵

Kinetics and Determination of the Rate-Controlling Step. To investigate the kinetics of leaching, a test was conducted using the optimized conditions for molybdenum recovery. The test aimed to analyze the rate at which leaching

occurred within the specified time frame. The shrinking core model is the most commonly used model for describing the kinetics in leaching processes.³² The shrinking core model employed in this work accounts for consecutive steps in the leaching process, including the diffusion of the reagent through a liquid film surrounding the particles, the diffusion through a solid product layer surrounding the particles, and the dissolution reaction taking place on the surface of the unreacted core, leading to metal mobilization. For each step, there are corresponding kinetic equations (eqs 6–8) that describe the rate of the process. The equation that best fits the experimental data is considered to be the rate-controlling step.²³

Film diffusion control:

$$t \propto X \quad (6)$$

Product layer diffusion control:

$$t \propto 1 - 3(1 - X)^{2/3} + 2(1 - X) \quad (7)$$

Chemical reaction control:

$$t \propto 1 - (1 - X)^{1/3} \quad (8)$$

where t is the reaction time and X is the fraction of leached metal. The kinetic data obtained from the different mechanism equations (eqs 6–8) are presented in Figure 6a. The plot clearly indicates a change in slope at approximately 5 min for each equation, suggesting a shift in the leaching mechanism at this point. Therefore, the kinetic data needs to be analyzed in two steps. In the first step, encompassing the initial 5 min, eqs 6–8 were utilized, and the corresponding kinetic plots are displayed in Figure 6b. The plot demonstrates that the chemical reaction control equation exhibits the highest R^2 value, indicating its dominance at this stage. The value of the rate constant for chemical control kinetics up to 5 min is 0.06 min^{-1} . However, it is worth noting that film and product layer diffusion processes also occur concurrently to some extent. To explore the kinetics of the second step, which begins at 5 min and onward, a new set of equations derived by Aarabi-Karasgani et al. are employed.³³ Equations 9–11 are the equations for film diffusion, product layer diffusion, and chemical reaction control, respectively. These equations capture the behavior of the leaching process beyond the initial 5 min period:

$$X - X_1 \propto X \quad (9)$$

$$t - t_1 \propto 3[(1 - X_1)^{2/3} - (1 - X)^{2/3}] - 2(X - X_1) \quad (10)$$

$$t - t_1 = (1 - X_1)^{1/3} - (1 - X)^{1/3} \quad (11)$$

where X is the fraction of leached metal in the second stage, t_1 is the time at which the second stage is started, and X_1 is the fraction of leached material at time t_1 . R^2 values observed in Figure 6c are very close to each other for liquid film, product layer diffusion, and chemical control. Therefore, kinetics is probably governed by a mixed control mechanism.^{32,34} For this reason, the rate constant was calculated as an average of each mechanism with a value of 0.018 min^{-1} .

CONCLUSIONS

A simple, efficient, and sustainable process was developed to recover molybdenum from a specific spent catalyst. Tartaric acid is sourced from winery waste and employed in the leaching of the spent molybdenum catalyst. This approach allows for the recovery of secondary raw materials from industrial solid waste by utilizing another material generated by the winery industry. Furthermore, when tartaric acid is compared to inorganic acids, it has a lower environmental impact. The use of organic acids, as tested in this work, allows for the efficient extraction of molybdenum. The latter eliminates the need for hard acids or bases, which can be hazardous to both the process and the operators. Furthermore, the use of organic acids derived from agrifood waste not only reduces waste production, but also makes it possible to recover the valuable metal of molybdenum. The reproducibility of the developed process was studied, and the results indicated a molybdenum recovery rate of $87.36\% \pm 2.94$ under the optimal conditions previously determined: 1.3 M of tartaric acid, 75 g/L of solid–liquid ratio, a reaction time of 60 min, and a temperature of $25 \text{ }^\circ\text{C}$. The SCM demonstrated a good fit with the experimental data, allowing for the determination of the rate constant for the leaching process. It was possible to accurately describe the kinetics of the process and extract

meaningful information about the rate at which the desired reaction occurs. From an economic standpoint, evaluating the market price of tartaric acid in comparison to the commonly used inorganic acid in hydrometallurgy (e.g., H_2SO_4), the developed process using tartaric acid would be more expensive. Nevertheless, if tartaric acid is sourced from agrifood waste and integrated into a circular economy, this would significantly lower the cost and render the process more economically viable.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c04318>.

Elemental microanalysis, FT-IR analysis, TGA/DTA analysis, and XRD analysis (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Prakash, S.; Tuli, G. D.; Basu, S. K.; Madan, R. D. *Advanced Inorganic Chemistry*; S. Chand Publishing, 2006; Vol 2.
- (2) Grohol, M.; Veeh, C. European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship Study on the critical raw materials for the EU 2023. Final report, Publications Office of the European Union, 2023, <https://data.europa.eu/doi/10.2873/725585>.

- (3) Kar, B. B.; Datta, P.; Misra, V. N. Spent catalyst: Secondary source for molybdenum recovery. *Hydrometallurgy*. **2004**, *72* (1–2), 87–92.
- (4) IMO. Mining and processing. <https://www.imoa.info/molybdenum/molybdenum-mining.php> (accessed 28-08-2023).
- (5) Vemic, M.; Bordas, F.; Guibaud, G.; Lens, P. N. L.; van Hullebusch, E. D. Leaching and Recovery of Molybdenum from Spent Catalysts. *Sustainable Heavy Metal Remediation*. **2017**, 207–239.
- (6) Brookes, C.; Bowker, M.; Wells, P. P. Catalysts for the selective oxidation of methanol. *Catalysts* **2016**, *6* (7), 92.
- (7) Malik, M. I.; Abatzoglou, N.; Achouri, I. E. Methanol to formaldehyde: An overview of surface studies and performance of an iron molybdate catalyst. *Catalysts* **2021**, *11* (8), 893.
- (8) Global Formaldehyde Industry. Globenewshire publication, 2022. <https://www.globenewswire.com/news-release/2020/07/08/2059521/0/en/Global-Formaldehyde-Industry.html> (accessed 10-07-2023).
- (9) Kar, B. B.; Datta, P.; Misra, V. N. Spent catalyst: Secondary source for molybdenum recovery. *Hydrometallurgy*. **2004**, *72* (1–2), 87–92.
- (10) Gao, B.; Jiang, H.; Zeng, M.; Peng, M.; Hu, L.; Zhang, W.; Mao, L. High-efficiency recycling method for Mo and Ni from spent catalyst via soda roasting and solvent extraction. *J. Clean Prod.* **2022**, *367*, 132976.
- (11) Zhang, M.; Song, H.; Zheng, C.; et al. Highly efficient recovery of molybdenum from spent catalyst by optimized process. *J. Air Waste Manage Assoc.* **2020**, *70*, 971–979.
- (12) Akcil, A.; Vegliò, F.; Ferella, F.; Okudan, M. D.; Tuncuk, A. A review of metal recovery from spent petroleum catalysts and ash. *Waste Management*. **2015**, *45*, 420–433.
- (13) Monjezi, M.; Shahriar, K.; Dehghani, H.; Samimi Namin, F. Environmental impact assessment of open pit mining in Iran. *Environmental Geology*. **2009**, *58* (1), 205–216.
- (14) Yao, Z.; Xu, Z.; Shuai, Q. Solidification of municipal solid waste incineration fly ash through co-mechanical treatment with circulation fluidized bed combustion fly ash. *Materials* **2020**, *13* (1), 141.
- (15) IMO. Molybdenum market information. <https://www.imoa.info/molybdenum/molybdenum-global-production-use.php> (accessed 10-07-2023).
- (16) Kontogiannopoulos, K. N.; Patsios, S. I.; Karabelas, A. J. Tartaric acid recovery from winery lees using cation exchange resin: Optimization by Response Surface Methodology. *Sep Purif Technol.* **2016**, *165*, 32–41.
- (17) Devesa-Rey, R.; Vecino, X.; Varela-Alende, J. L.; Barral, M. T.; Cruz, J. M.; Moldes, A. B. Valorization of winery waste vs. the costs of not recycling. *Waste Management*. **2011**, *31* (11), 2327–2335.
- (18) Rezki, A. S.; Sumardi, S.; Astuti, W.; Made Bendiyasa, I.; Petrus, H. T. B. M. Molybdenum Extraction from Spent Catalyst Using Citric Acid: Characteristic and Kinetics Study. *IOP Conference Series: Earth and Environmental Science* **2021**, *830*, 012020.
- (19) He, L. P.; Sun, S. Y.; Mu, Y. Y.; Song, X. F.; Yu, J. G. Recovery of Lithium, Nickel, Cobalt, and Manganese from Spent Lithium-Ion Batteries Using L-Tartaric Acid as a Leachant. *ACS Sustain Chem. Eng.* **2017**, *5* (1), 714–721.
- (20) Cucciniello, R.; Intiso, A. La Valorizzazione Dei Sottoprodotti Della Filiera Vitivinicola, 2021. <http://www.oiv.int/oiv/>.
- (21) Altomare, A.; Cuocci, C.; Giacobuzzo, C.; Moliterni, A.; Rizzi, R. QUALX: A computer program for qualitative analysis using powder diffraction data. *J. Appl. Crystallogr.* **2008**, *41* (4), 815–817.
- (22) Altomare, A.; Corriero, N.; Cuocci, C.; Falcicchio, A.; Moliterni, A.; Rizzi, R. QUALX2.0: A qualitative phase analysis software using the freely available database POW-COD. *J. Appl. Crystallogr.* **2015**, *48*, 598–603.
- (23) Mahandra, H.; Ghahreman, A. A sustainable process for selective recovery of lithium as lithium phosphate from spent LiFePO₄ batteries. *Resour Conserv Recycl.* **2021**, *175*, 105883.
- (24) Zollfrank, C.; Gutbrod, K.; Wechsler, P.; Guggenbichler, J. P. Antimicrobial activity of transition metal acid MoO₃ prevents microbial growth on material surfaces. *Materials Science and Engineering C* **2012**, *32* (1), 47–54.
- (25) Kostromina, N. A.; Trunova, E. K.; Tananaeva, N. N. Complex formation of Fe(III) with tartaric acid by the method of nuclear magnetic relaxation. *Theoretical and Experimental Chemistry* **1988**, *23*, 462–466.
- (26) Yokoi, H.; Mitani, T.; Mori, Y.; Kawata, S. Complex formation between iron (III) and tartaric and citric acids in a wide pH range 1 to 13 as studied by magnetic susceptibility measurements. *Chem. Lett.* **1994**, *23* (2), 281–284.
- (27) Rohwer, E. A.; Cruywagen, J. J. A Comparative Study of the Complex Formation of Molybdenum(VI) and Tungsten(VI) with Ligands Derived from Carboxylic Acids, 2000. <http://scholar.sun.ac.za>.
- (28) Cavaleiro, A. M. V. S. V.; Gil, V. M. S.; Pedrosa de Jesus, J. D.; Gillard, R. D.; Williams, P. A. NMR Studies of Complexes of Molybdenum(VI) with Tartaric Acid in Aqueous Solution. *Transitions Metal chemistry*. **1984**, *9*, 62–67.
- (29) Cuin, A.; Massabni, A. C. Synthesis and characterization of solid molybdenum(VI) complexes with glycolic, mandelic and tartaric acids. Photochemistry behaviour of the glycolate molybdenum complex. *J. Coord. Chem.* **2007**, *60* (18), 1933–1940.
- (30) Jha, M. K.; Kumari, A.; Jha, A. K.; Kumar, V.; Hait, J.; Pandey, B. D. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. *Waste Management*. **2013**, *33* (9), 1890–1897.
- (31) Ye, R.; Zhao, Z.; Gao, R.; Wan, J.; Cao, X. Conversion of Calcium Citrate to Citric Acid with Compressed CO₂. *ACS Omega*. **2022**, *7* (1), 683–687.
- (32) Levenspiel, O. *Chemical Reaction Engineering*; Wiley, 1998.
- (33) Aarabi-Karagani, M.; Rashchi, F.; Mostoufi, N.; Vahidi, E. Leaching of vanadium from LD converter slag using sulfuric acid. *Hydrometallurgy*. **2010**, *102* (1–4), 14–21.
- (34) Faraji, F.; Alizadeh, A.; Rashchi, F.; Mostoufi, N. Kinetics of leaching: A review. *Reviews in Chemical Engineering*. **2022**, *38*, 113–148.